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The use of Dihexyldithiocarbamate in Solvent Extraction of Transition Metals

Soja Siti Fatimah[a,b], Husein H. Bahti[b,*], Iwan Hastiawan[b], Anna Permanasari[a], and Evamarie Hey-Hawkins[c]

[a]*Department of Education Chemistry, Faculty of Mathematics and Natural Sciences Education, Indonesia University of Education Jl. Dr. Setiabudhi No. 229, Bandung 40154, Indonesia.*

[b]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University, Jl. Raya Bandung-Sumedang, Km. 21, Jatinangor 45363, Indonesia.*

[c]*Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany.*

Abstract

Dialkyldithiocarbamates have long been used as chelating agents in solvent extraction of transition metals. In our previous study, an alkyl homolog of this type of ligand, namely dihexyldithiocarbamate (DHDTC), was synthesized and characterized. The use of this particular ligand in the extraction some selected transition metal ions is now reported for the first time. The effect of pH, of the metal to the ligand mole ratio, and of the variation in organic solvents, in the extraction of Fe^{3+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}, were investigated. Results of the experiments showed that an extractability of about 44.62%, 58.15%, and 61.69%, respectively for Ni^{2+}, Zn^{2+}, and Cd^{2+} at pH 8 could be achieved. For Cu^{2+} and Fe^{3+} at pH 5 (69.96%) and pH 9 (81.29%). The metal to the ligand mole ratio for divalent transition metal, was 1:2 while trivalent was 1:3.

Keywords: Dihexyldithiocarbamic acid; solvent extraction; transition metals.

*Corresponding author
E-mail address: husein.bahti@unpad.ac.id

1. Introduction

Major advances in the synthesis of derivative compounds from dithiocarbamate have been made, recently. These compounds are attractive because of their potential applications and use in a wide range of fields, such as in rubber industry for vulcanization additives, inhibitors for enzymatic reactions[1-3], photoelectronics, adsorbents, catalysts[4-6], agents for pesticides, and for chelating agents[6-9].

As chelating agents, dithiocarbamate derivatives have been of a great interest. Many papers described that these derivative compounds reacted with many metal ions to form chelate complexes. Dilli and Hutchins[10] reported that dialkyldithiocarbamates reacted with Zn(II), As(III), Fe(III), Cd(II), Ni(II), Cu(II), Hg(II), Co(II) and Cr(III) to form complexes. Schwedt (1979)[11] reported that tetrametylendithiocarbamate, reacted with Cd(II), Pb(II), Ni(II), Co(II), Zn(II), Cu(II), and Hg(II).

The purpose of this study was to use dihexyldithiocarbamate for solvent extraction of transition metals. With

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dithiocarbamates having longer alkyl groups in their molecular structure, such as hexyl, it's expected that the ligand would have better properties to be used in the extraction of transition metal ions.

2. Experimental

2.1 Materials and Equipments

Dihexylamine was obtained from Alfa-Aesar while carbon disulphide was from Sigma Aldrich. Potassium hydroxide was purchased from Merck. All chemicals used were of analytical or higher purity grade. Solvents were used without further purification. A Consort C380 pH meter was used for all pH measurements. Quantitative analyses for transition metal ions were done using a Perkin Elmer Analyst 100 atomic absorption spectrometer.

2.2 Preparation of the ligand dihexyldithiocarbamate, and its solution.

Preparation of dihexyldithiocarbamate were performed following procedure[12] with modification. Dihexylamine (11.7 mL) and metanol (15 mL) in a 250 mL round bottom flask was cooled on ice. Into the cool liquid, carbon disulphide (3 mL) was added drop by drop, with a constant stirring. Pottasium hydroxide solution was subsequently added into the reaction mixture, which was stirred for until a pale yellow precipitate was formed. Preparation ligand conducted in Schlenk-line using liquid nitrogen. The precipitate was collected and then, diluted with methanol. Those processes above were conducted twice to get purify precipitate. The purified precipitate was dried in a vacuum desicator.

A solution of the ligand (3.34 mol) was prepared by dissolving 1g of dihexyldithiocarbamate in 100 mL of methanol.

2.3 Extraction Procedure

Extraction of transition metals experiments were performed following the existing procedure. A mixture of an aqueous solution of metal ion (10 mL), a phosphat buffer solution (4 mL), and a solution of the ligand in methanol (1 mL) in a separating funnel was vigorously agitated using a mechanical shaker for 15 min. The reaction mixture was extracted by shaking with an organic solvent (toluene, *n*-hexane, or diethyl ether; twice; 7.5 mL) for 30 minutes. After standing the extraction mixture for a few minutes, the organic phase was transferred, and the aqueous phase was analyzed for its remaining metal ion content using atomic absorption spectrometry.

3. Results And Discussion

Extraction experiments were carried out on solutions of 5 selected transition metal ions; Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Fe^{3+}, at initial concentration of about 100 ppm, in the pH range of 4 to 9 (see Table 1).

Tabel 1. Data on extraction of some transition metals as dihexyldithiocarbamate at a pH range of 4-9, and ligand 1% in methanol, toluene as organik solvent.

Metals ion		Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Fe^{3+}
Initial concentration (ppm)		107.4	110.8	94.1	100.0	94.4
pH	4	72.40	47.14	56.03	39.56	65.80
	5	63.10	33.24	53.63	39.43	39.45
	6	67.50	42.25	52.35	40.23	39.65
	7	72.40	50,57	54.12	48.95	40.34
	8	59.46	36.23	39.36	38.48	52.14
	9	68.20	36.62	54.77	44.56	17.70

From the resulted data (not presented in this report) it was found that from the three organic solvents (diethyleter, *n*-hexena, and toluene) investigated in the preliminary extraction study, toluene gave the best extraction efficiency. Thus, toluene was used as the solvent throughout the rest of the extraction study.

The data in Table 1 show that decreasing in concentrations to about 60% of their initial concentration of Cu^{2+}, Cd^{2+}, Zn^{2+},less 60% of Ni, and to more than 80% of Fe^{3+} could be achieved by one equilibration of aqueous phase with organic phase, at a pH range of 4–9. To what extent of extraction of a metallic ion with a ligand, can be

understood from the general reaction equation between a metal ion (M^{n+}) and a ligand (L^-) to form a complex molecule (M_xL_n), as follow:

$$H_2O + M^{n+}(aq) + L^- (org) \leftrightharpoons M_xL_n(org) + nH_3O^+(aq) \quad (1)$$

Increasing the mol ratio of the ligand to metal ion, or adding the amount of ligand in excess may probably increase the stability of the complexes and thus the extractability of the metal ions. Or, increasing the concentration of the ligand will tend to shift the equilibrium of the reaction to the formation of neutral complex molecule, and will in turn increase the solubility of the complex in organic phase.

Table 2 below presents data on distribution ratio of the metal ions under investigation in the extractions. Distribution ratio D is defined as the ratio between the concentration of the complex molecule in the organic phase and the concentration of the metal ion remaining in the aqueous phase, during extraction precess.

$$D = \frac{[M_xL_n]org}{[(M^{n+})]aq} \quad (2)$$

For a good extraction efficiency the value of D should be greater than 1.000. Based on this criterion, and on the data in Table 2, it can be expected that a good extraction efficiency could be achieved in the extraction of Cu^{2+}, Cd^{2+}, Zn^{2+} and Fe^{3+}.

Tabel 2. Distribution ratio of transition metals in solvent extraction

Metals~pH		Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Fe^{3+}
$[M^{n+}]$ initial (ppm)		107.4	110.8	94.1	100.0	94.4
pH	4	0.483	1.350	0.679	1.527	0.435
	5	0.591	2.333	0.754	1.536	1.392
	6	0.591	1.622	0.797	1.485	1.381
	7	0.483	1.191	0.738	1.042	1.340
	8	0.806	2.058	1.390	1.598	0.810
	9	0.575	2.025	0.718	1.244	4.333

The extractability of the metal ion can be explained theoretically as follows: The $NCSS^-$ groups on dithiocarbamate and homologous alkyl groups that they are attached to increases the extraction ability of these ligands due to the soft donor structure of the NCSS and causes big affinity to soft ion metals (Cd^{2+}). Fe^{3+} is ion hard atom but has ion charge more than others. Ni^{2+}, Cu^{2+}, Zn^{2+} is borderline.

As can be seen in Table 2 and Table 3, extraction to organic phase increases as pH increases. The reaction equation also tells that the extent of extraction is a pH dependent, because formation of complex molecule involves a generation of protons. It is interesting to note that extraction efficiency at pH 9 was much higher for Fe^{3+}, than any other metals studied.

Tabel 3. Percent extraction of several metals ions using dihexyldithiocarbamate as the ligand.

Metals	% Extraction					
	pH~4	pH~5	pH~6	pH~7	pH~8	pH~9
Ni^{2+}	32.56	37.14	37.14	32.56	44.62	36.50
Cu^{2+}	57.44	69.96	61.83	54.33	67.21	66.88
Zn^{2+}	40.65	43.08	44.52	42.65	58.15	41.98
Cd^{2+}	60.59	71.44	59.87	51.07	61.69	55.53
Fe^{3+}	30.41	58.24	58.02	57.26	44.75	81.29

[a] H_2O/C_6H_5 =15/15 (v/v) [ligand] = 3.3x 10^{-2}, 298K, 1h contact time

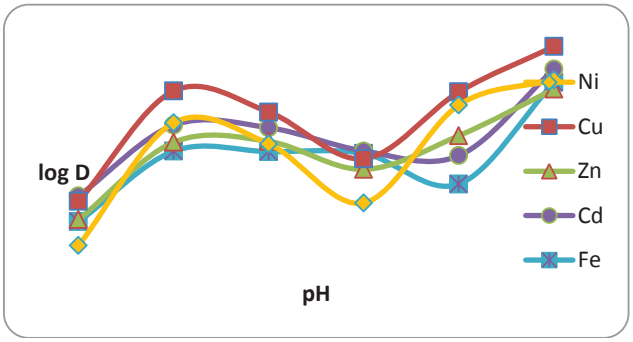

Fig. 1. pH-log D graph of dihexyldithiocarbamate

When pH increases, distribution coefficient has to increase too. But as the structure of ligands does not suit the general mechanism, logarithmic curves are observed. The slopes of linear parts of pH-log D graph are usually in fractional numbers. According to Karapinar *et al*. (1997)[13], as certain parts of these graphs show protonation or deprotonations while descending parts show metal hydrolyses. However, according to some author all the experimentas were done to calculate pH curves resulting in different shaped curves in each trial.

To determine of the metal to the ligand mol ratio, extraction of Cd^{2+}, Zn^{2+}, into toluene at different concentrations of dihexyldithiocarbamic acid at pH of 8, pH 9 for Fe^{3+} was performed, and the resulted data are presented in Figure 2 below.

As can be inferred from the curves in Figure 3 based on slope rasio method, the ratio of metal-ligand for divalent transition metals (Cd^{2+}, and Zn^{2+}) is 1 : 2 while Fe^{3+} is 1:3. Characterization of solvent extraction of transition metals with dihexyldithiocarbamate not reported so far.

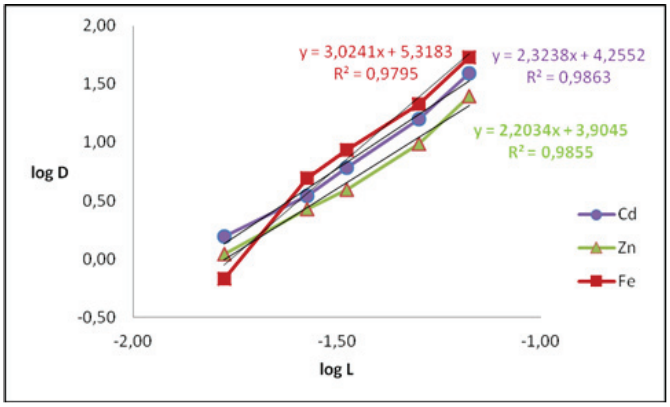

Fig. 2. Plots of log D versus log L for divalent and trivalent transition metals of DHDTC.

Conclusions

Extraction of transition metal ions could be best done using toluene as the organic phase. The effectiveness of extraction of Ni^{2+} , Zn^{2+} , and Cd^{2+} with dihexyldithiocarbamate at a pH of 8 were 44,62% , 58,15%, and 61,69%, consecutively, while for Cu^{2+} $^{+}$ at pH 5 was 69,96% and for Fe^{3+} at pH 9 was 81,29%. The metal to the ligand mole ratio for divalent transition metals studied was 1:2, while for the trivalent metal was 1:3.

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